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Mycoremediation of heavy metal pollution: A review

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Abstract
Heavy metal pollution of the environment is one of the biggest issues of today's society. Whether it affects soils or water, once introduced in the environment, heavy metals cannot be biodegraded. In agriculture, heavy metal pollution affects both the quality and the quantity of the crops. In the aquatic environment, heavy metals affects not only the aquatic life but also it affects human directly, through the contamination of the drinking water. Their presence in environment results in bioaccumulation, further affecting biological and ecological cycles. Mining activities, chemical weathering of minerals, leather and textile industry and industrial discharges are just a few examples of heavy metals pollution sources. However, some heavy metals have importance as trace elements, for the growth and development of organisms such as plants and fungi. Due to their persistence in environment, microorganisms have evolved mechanisms to tolerate heavy metals presence through adsorption or chemical reduction of metal ions. In fact, the role of fungi as decomposers in the ecosystems led to the studying of their enzymes and ability to mycoremediate heavy metals. To obtain mycoremediation of heavy metal pollution, the aim is to determinate the right fungal species to target a specific pollutant. This paper aims to review the potential of fungi to bioremediate heavy metal pollution.

Keywords: mycoremediation, bioaccumulation, fungi, heavy metal pollution, environment

1. INTRODUCTION

Heavy metal is a term generally used for the group of metals that have the density greater than 5 g/cm^3 [1]. Although is a relatively defined term, it is generally recognized and applied to the widespread contaminants of terrestrial and freshwater ecosystems [2]. Heavy metals include arsenic (As), lead (Pb), zinc (Zn), cadmium (Cd), chromium (Cr), mercury (Hg), copper (Cu), iron (Fe), silver (Ag) and other metals or metalloids. These metals occur naturally in rocks, soils, sediments and water in a natural background concentration, but due to human activity there is an increase of those concentrations. Since heavy metals cannot be degraded, they persist and accumulate in the environment. A pollutant is any substance in the environment, which causes objectionable effects, impairing the welfare of the environment, reducing the quality of life and may eventually cause death [3]. Therefore, environmental pollution refers to the presence of a pollutant in the air, water, soil, in concentrations over the acceptable

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limit, that may be toxic or poisonous and will cause harm to living things in the polluted environment [3].

The global development of industries and urbanization led to an increase in the concentrations of those pollutants. Sources of heavy metals vary from activity to activity. Mainly, metals are released during mining activities. In some cases, the emitted metals continue to persist in the environment, even after the mining ceased. For example, after gold exploitation, arsenic can persist over time, even when the concentration of other trace metals in the solution decreases due to natural attenuation [4]. Sources of metal contamination can be divided in five main groups: metalliferous mining and smelting, industry, atmospheric deposition, agriculture and waste disposal [2]. Regardless of the source of pollution, heavy metals may end up in solid or liquid waste during the phases of the production process.

2. TYPES OF POLLUTION

2.1. Air pollution

Regarding air pollution, both human and natural sources are responsible for the increase of heavy metals in the air. Nevertheless, manmade sources of atmospheric emissions exceed the natural ones for the most metals. Sometimes, even the metals that are present in wind-blown dusts have an industrial origin. A few examples of heavy metals sources of air pollution are: automobile exhaust, insecticides, fossil fuel industry (e.g. burning coal), manufacturing of steel, etc. Furthermore, emission of metals into the air may also contaminate soils or aquatic ecosystems through atmospheric fallout.

2.2. Water pollution

Water pollution occurs at the industrial production level and also with the end use of the products and run-off. Sources of heavy metals sources of water pollution are shown in ***Table 1***.

Table 1 Heavy metals sources in water pollution (Verma and Dwivedi, 2013)

Heavy metal	Source
Chromium (Cr)	Mining, industrial coolants, chromium salts manufacturing, leather tanning
Lead (Pb)	Lead acid batteries, paints, E-waste, smelting operations, coal-based thermal power plants, ceramics, bangle industry
Mercury (Hg)	Chlor-alkali plants, thermal power plants, fluorescent lamps, hospital waste (damaged thermometers, barometers, sphygmomanometers), electrical appliances etc.
Arsenic (As)	Geogenic/natural processes, smelting operations, thermal power plants, fuel
Copper (Cu)	Mining, electroplating, smelting operations
Vanadium (Va)	Spent catalyst, sulphuric acid plant
Nickel (Ni)	Smelting operations, thermal power plants, battery industry
Cadmium (Cd)	Zinc smelting, waste batteries, E-waste, paint sludge, incinerations & fuel combustion
Molybdenum (Mo)	Spent catalyst
Zinc (Zn)	Smelting, electroplating

All of these sources of pollution affect the chemical characteristics of the water, sediments and aquatic life. The pathways of water contamination are either directly, by willingly discharging industrial wastewater in the freshwater bodies or through leaching from agriculture soils, malfunctioning factories, accidents, etc.

Due to accelerating global development and industrialization there is an increase in the rate at which heavy metals are released into the environment, having the effect of alterating many of the freshwater bodies. As example, increasing human development in the watershed, municipal and industrial wastes

added trace metal to the Mississippi River (USA) and Lake Pepin [2]. Likewise, the great Ganges of India also has been found to have high heavy metals in sediments and fish [2], due to the discharges of municipal and industrial wastes. Many of those changes affects not only the aquatic life but pose a serious risk for human health. One of the ways humans get contaminated with heavy metals is through contaminated water and fish consumption. Fish living in polluted waters tend to accumulate heavy metals in their tissues [5]. Generally, metals accumulate in liver, kidney and gills, and the level of accumulation depends on water pH, temperature, salinity, metal concentration, time of exposure, way of metal uptake, fish age and feeding habits [5].
Symptoms and diseases associated with human exposed to high heavy metals concentrations are shown in ***Table 2***.

Table 2 Medical conditions associated with high heavy metals concentration in humans (Fernandez-Luqueno *et al.*, 2013)

Heavy metal	Exposure route	Symptoms or diseases
Arsenic	Water ingestion	Melanosis, leucomelanosis, effects on neuronal development, damage to DNA, cerebrovascular diseases, diabetes, kidney diseases, lesions on skin and liver, chronic renal failure, cytogenic damage
	Water consumption	Lung function failure and skin lesions
	Water and food ingestion	Lesions on heart, gangrene, diabetes mellitus, hypertension, and ischemic heart disease
	Ingestion	Alterations on the gene expression
	Smoking cigarettes and water ingestion	Coughing, chest sounds in the lungs and shortness of breath
Bismuth	Food consumption	Liver and kidney failure
	Nanoparticles	Pneumoconiosis, myocardial infarction
	Food consumption	Accumulation in liver, gills and muscles
Cadmium	Ingestion	Kidneys failure
	Water ingestion	Chronic renal failure, it is absorbed via the alimentary tract, penetrates through placenta during pregnancy, risks of stillbirth, and damages membranes and DNA
Cerium	Nanoparticles, ingestion and inhalation	Toxicity
	Soil, inhalation, dermal contact	Cancer
Chromium	Water ingestion, meat	Stomach cancer
Cobalt	Water ingestion	Accumulation in muscle, liver and gills

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Copper	Ingestion and dermal contact	Alzheimer type II astrocytosis, cognitive dysfunction and ataxia
Gallium	Occupational exposure, ingestion	Pulmonary toxicity
Gold	Mining	Pneumotitis, headache, gastro-intestinal bleeding
	Inhalation, water ingestion	Toxicity, Alzheimer type II astrocytosis, cognitive dysfunction and ataxia
Iron	Water ingestion	Accumulation in muscle, liver and gills
	Food consumption	Brain damage and reduction of mental processes
	Ingestion	Lower energy levels
Lead	Ingestion and inhalation	Blood composition, Parkinson disease, neurodegenerative disorders
	Water ingestion	Chronic renal failure
Manganese	Ingestion	Alzheimer type II astrocytosis, cognitive dysfunction and ataxia
	Water ingestion	Effects on central nervous functions
Mercury	Water ingestion	Damage to DNA, accumulation in muscle, liver and gills
Nickel	Food and water ingestion, inhalation	Allergies and cancer, cancer of the lungs, throat, stomach, nose and sinuses
Platinum	Water ingestion and vegetables	Accumulation in tissues
Silver	Water and food ingestion	Decreases blood pressure, stomach irritation and decreased respiration
Thallium	Food, vegetables	Fetal demise, causes adverse health effects and degenerative changes in many organs
Tin	Occupational exposure, inhalation, ingestion	Lung cancer, cancer and chronic kidney diseases
Uranium	Water ingestion	Renal dysfunction
Vanadium	Water ingestion	Cirrhosis, renal stone disease, hypokalemic periodic paralysis and cancer
Zinc	Water ingestion, food consumption	Accumulation in muscle, liver and gills

The discharge of heavy metals into water sources can also lead to physical, chemical, and biological disorders, generating changes in diversity, density, species composition of population, and structure of the community [6].

2.3. Soil pollution
Due to rapid industrialization and population expansion, the quantity of industrial and municipal waste and other pollutants increased in many countries. The level of soil pollution by heavy metals depends

on factors such as the soil retention capacity, composition, organic matter and grain size and also on the chemical properties of the metal [2]. Metals may be retained by soil components at the surface, may precipitate or co-precipitate as sulfides, carbonates, oxides or hydroxides with Fe, Mn, Ca, etc. [2]. Therefore, soil contamination may be at the surface of it, and also in the deeper layers. Thereby, when entering the soil in large concentrations, heavy metals affects microorganisms reducing their populations, activity and species diversity. Likewise, the activity of soil enzymes decreases and humus content, structure and pH are changed [2]. All of those processes eventually lead to partial or complete loss of soil fertility, affecting therefore not only crop yields in agriculture industry but the ecosystem itself. In the same way, when taken up by plants, heavy metals may enter the food chain and pose serious risks to human health. Crops grown near busy roads or industrial plants, or crops exposed to municipal and industrial waste are more prone to have a higher heavy metals concentration.

3. BIOREMEDIATION OF HEAVY METAL POLLUTION

Since microorganisms have developed various strategies for their survival in heavy metal-polluted habitats, these organisms are known to develop and adopt different detoxifying mechanisms such as biosorption, bioaccumulation, biotransformation and biomineralization, which can be exploited for bioremediation [7]. Fungi have a unique ability to degrade cellulose, hemicellulose and lignin (compounds which are found in plants, giving their structure). Beside this, fungi have both ecological adaptability and biochemical capability to decompose pollutants and reduce the threat of these pollutants by either chemically modifying their chemical structure or by affecting their bioavailability [8]. Lately, fungal organisms have been used efficiently as biosorbents for the removal of heavy metals from polluted soil and water. They help to transform metal contaminants to soluble and insoluble forms through several biological mechanisms; mechanisms which are part of the biogeochemical cycling of substances and are important for both ex situ and in situ bioremediation processes [8].

In the presence of heavy metals, fungi either are affected negatively (inhibition of growth, death of the fungus or reduced metabolic rate) or positively (are not or less affected by the heavy metals). The way that fungi interact positively with heavy metals is the base of how removal of heavy metals from wastewater and soil should be approached.

The researchers have reported a number of fungi having multi-metal removal capacity in growing/viable form and in the dead biomass form of the fungi [9]. A selection of the heavy metal tolerant fungi is shown in ***Table 3.***

Table 3 Heavy metal tolerant fungi (after Kumar and Dwivedi, 2021)

Class of fungi	**Name of the fungi**	**Name of the pollutants**
Ascomycetes	*Aspergillus flavus*	Cu, Pb, Cr, Cd
	Aspergillus niger	Cu, Pb, Cr, Zn, Cr, Ni, V
	Beauveria bassiana	Zn, Cu, Cd, Cr, Ni
	Penicillium simplicissimum	Cd, Pb, Cu, Zn, Cr
	Aspergillus fumigatus PD-18	Cd, Cr, Ni, Pb, Zn
	Neurospora sp.	Pb, Ni, Co, Cr, Cu, Zn
Basidiomycetes	*Flammulina velutipes*	Cu, Zn, Hg
	Fomitopsis meliae	Cd, Cu, Pb, Fe
	Pleurotus eryngii	Cu, Zn, Hg
	Pleurotus ostreatus	Cu, Zn, Hg, CdS
Deuteromycetes	*Alternaria sp.*	Ni, Cd
Zygomycetes	*Mucor indicus*	Pb
	Rhizomucor pusillus	Pb, Cr, Cd
	Rhizopus microspores	Cd, Cu, As, Fe

In remediation of heavy metals, fungi have been used in two ways: in growing form and in dead biomass form [9]. In viable/growing form, the fungus should have a tolerance ability towards pollutants because heave metals may be toxic in nature and can inhibit the growth of the fungi [9]. In a study conducted by Sanglimsuwan *et al.* [10] for the fungi resistance to metals (Cu, Cd, Zn, Ni, Co and Hg), out of 21 strains, the most resistant were *P. ostreatus* and *P. cystidiosus.* Hassan *et al.* [8] found that *Aspergillus fumigatus* was the most tolerant to As, and other fungi with high tolerance were *P. subtephrophora, A. niger* and *C. aurantiopora.* In their study they observed that beside physiochemical properties and pH of the soil, above mentioned fungi strains had equally played a role in the process of bioremediation of heavy metals. Khan *et al.* [11] presented in their study that isolates *Aspergillus fumigatus*, *Penicillium rubens*, and *Aspergillus niger* showed higher efficiency for Cd removal with 79%, 98% and 98% in SDB (Sabouraud Dextrose Broth) medium, while the lowest efficiency, 76%, 75%, and 79%, was observed in CYE (Charcoal-Yeast Extract) medium. The maximum (0.465 mg g^{-1}) uptake efficiency for Cd removal from heavy-metal contaminated soil was noticed for *Aspergillus fumigatus* M3Ai strain grown on SDB medium, while the lowest uptake efficiency of this strain was 0.450 mg g^{-1} with CYE medium [11]. *Penicillium rubens* M2Aiii strain had the highest uptake efficiency as 0.575 mg g^{-1} with SDB medium and the lowest uptake efficiency was 0.441 mg g^{-1} with CYE medium; and for the *Aspergillus niger* M1DGR strain, the maximum uptake efficiency for Cd removal was observed as 0.580 mg g^{-1} with CYE medium, and the lowest uptake efficiency was 0.464 mg g^{-1} with YPG (Yeast Extract – Peptone – Glycerol) medium [11]. For Cr removal, the maximum uptake efficiency was noticed for *Aspergillus niger* M1DGR strain when grown in SDB medium [11]. Likewise, the highest uptake efficiency of *Aspergillus fumigatus* M3Ai strain was observed as 0.40 mg g^{-1} with CYE medium, and the lowest uptake efficiency of this strain was 0.07 mg g^{-1} with SDB medium [11]. In another study, Bandurska *et al*. [12] tested the mycoremediation of soil contaminated with Cd and Pb by *Trichoderma sp.* The results of the study showed that the concentration of Pb ions decreased from 3000.0 to 130.9 µg/g on day 3 of growth period of the fungus *Trichoderma* in the culture medium, and 48.0 µg/g on day 15 of incubation [12]. Further, the concentration of Cd ions after 3 days of incubation was reduced from 300.0 to 7.3 µg/g; and incubation during 15 days increased the sorption of the Cd metal ions by the magnitude of 10 to 0.8 µg/g [12].

In another study, Kamal *et al.* [13] tested 19 fungal isolates for the removal of heavy metals. From these, fungal isolates named C1 and C3 showed the highest removal of 58.60% and 57.00% at 50 mg/L Cr concentration, followed by 53.80% and 50% at 100 mg/L, and the minimum removal of 46.3% and 42.2% at 200 mg/L Cr concentration under the optimized conditions [13]. For arsenic, the fungal isolates A2 and A6 showed the highest removal of 56.00% and 80.00% at 10 mg/L As concentration, followed by 53.20% and 67% at 50 mg/L [13].

Quader and Shekha's study [14] showed that *Aspergillus niger* has a higher removal percent for all concentrations of Pb were removed by (85.5, 85.33, 82.28, and 78.4%) and for Cd were (80, 79.26, 77.71 and 76.8%) [14].

4. CONCLUSIONS

The understanding of the mechanisms of heavy metals toxicity and how they interact with organisms is the key factor of their removal from contaminated soils, waters and air. Fungi presented a promising solution to the bioremediation of the heavy metals pollution, therefore further research will be a good opportunity to improve or develop novel biotechnological processes for this matter. Solutions may include blending native fungi strains to decontaminate polluted soils, using purified enzymes or genetically engineering of the fungi to improve their absorption rate. The full potential of fungi remains to be exploited, and further studies will help us expand the domains of applicability.

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